

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>H01L</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 00/30154</b> <b>(43) International Publication Date:</b> 25 May 2000 (25.05.00)
<b>(21) International Application Number:</b> PCT/US99/27092 <b>(22) International Filing Date:</b> 15 November 1999 (15.11.99)  <b>(30) Priority Data:</b> 60/108,656 16 November 1998 (16.11.98) US  <b>(71) Applicant:</b> RODEL HOLDINGS, INC. [US/US]; Suite 1300, 1105 North Market Street, Wilmington, DE 19899 (US).  <b>(72) Inventors:</b> SENOO, Hiroyuki; 172 Ikezawa-cho, Yam- ato Kohriyama-shi, Nara (JP). YOSHIDA, Kouchi; 172 Ikezawa-cho, Yamato Kohriyama-shi, Nara (JP). NISHIDA, Yoshikazu; 172 Ikezawa-cho, Yamato Kohriyama-shi, Nara (JP). SACHAN, Vikas; 121 Brook Run, Hockessin, DE 19707 (US). LACK, Craig, D.; 438 Greenwood Drive, Wilmington, DE 19808 (US). KOINKAR, Vilas, N.; 123 Bromley Drive, Wilmington, DE 19808 (US). LAVOIE, Raymond, Lee, Jr.; 157 Long Drive, Elkton, MD 21921 (US). BURKE, Peter, A.; 104 Interlachen Court, Avondale, PA 19311 (US).  <b>(74) Agent:</b> BENSON, Kenneth, A.; Rodel Holdings, Inc., Suite 1300, 1105 North Market Street, Wilmington, DE 19899 (US).		<b>(81) Designated States:</b> CN, JP, KR, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> METHOD TO CONTROL FILM REMOVAL RATES FOR IMPROVED POLISHING IN METAL CMP		
<b>(57) Abstract</b>  A composition useful for a second step planarization of a metal, barrier layer, and a dielectric insulating layer structure is provided which comprises: water, colloidal silica particles with a primary particle size between 10 and 100 nanometers and a surface area of 20 to 600 m <sup>2</sup> /g, and an oxidizing agent.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## METHOD TO CONTROL FILM REMOVAL RATES FOR IMPROVED POLISHING IN METAL CMP

5 This application claims the benefit of Provisional Patent Application  
Serial No. 60/108,656 filed November 16, 1998.

### BACKGROUND OF THE INVENTION

#### 10 Field of the Invention

The invention described pertains to the polishing methods and slurry  
formulations used in the planarization of integrated circuit surfaces  
containing various films, most particularly those of a metal, a barrier layer,  
15 and an insulator.

#### Related Art

One of the critical requirements necessary in the production of  
20 increasingly complex and dense semiconductor structures is the ability to  
retain planarity. Without the ability to planarize, the complexity and  
density of the structures constructed on a semiconductor wafer are greatly  
limited. Chemical-Mechanical Planarization, or CMP, is an enabling  
technology in this area, since it has proved to be the most effective method  
25 used to planarize surface films on semiconductor substrates.

While the first applications of CMP technology focused on the  
polishing of dielectric films (i.e.,  $\text{SiO}_2$ ), polishing of metal structures used  
for circuit interconnects is increasing rapidly. Along with the increase in  
30 metal planarization is an inherent increase in the number of different films  
that are simultaneously polished. Most metal structures contain three  
different films: a conductive metal layer, a barrier (or liner) layer between  
the conductive metal layer and the adjacent dielectric layer, and a  
dielectric layer. It is often desirable for the removal rates of each film to  
35 differ from each other in order to induce planarity and maintain the  
integrity of the semiconductor structure during polishing. In a typical  
metal structure, for example, if the entire planarization step were to take  
place in one step of polishing, it would typically be desirable to have high  
removal rates of material for the metal and barrier layers, while having low  
40 removal rates for the dielectric layer.

However, while it is certainly desirable to limit the number of processing steps, there are often inherent difficulties associated with a one-step process that limit its usefulness. It has been found that the one-step process described above where there are low removal rates for the dielectric layer sometimes results in a polished dielectric layer with a very high level of scratches which are very difficult to remove.

## SUMMARY OF THE INVENTION

A method is provided for polishing a composite semiconductor structure containing a conducting metal interconnect layer, an insulating dielectric layer, and a barrier layer between the two: most preferably, a tungsten metal layer, a silicon dioxide dielectric layer, and a barrier layer of titanium and/or titanium nitride. The method involves a two-step polishing process: in the first step, the majority of the conducting metal layer is removed without removing significant amounts of either the barrier layer or the dielectric layer. In the second step, the metal interconnect remaining on the horizontal portions of the barrier layer and the barrier layer are removed without removing significant amounts of the dielectric layer, and without degrading the integrity of the remaining structure by significant removal of the remaining metal layer (commonly called "dishing" or "recess") or removal of significant amounts of the remaining dielectric layer (commonly called "erosion"). Slurry compositions useful for accomplishing the second step polishing comprise: water, colloidal silica particles with a primary particle size between 10 and 100 nanometers and a surface area of 20 to 600 m<sup>2</sup>/g, an oxidizing agent, and, optionally, a surfactant or compound which acts to suppress the rate of removal of the dielectric insulating layer.

## DESCRIPTION OF PREFERRED EMBODIMENTS

For a one-step process for planarizing a structure comprised of an insulating layer, a barrier layer, and a conductive metal layer, one would use a slurry which provides high removal rates for the metal and barrier layers and low removal rates for the insulating layer. In order to prevent dishing of the metal (plug, contact, or via) and scratching of the insulating layer, one must stop the polishing at the "just clear point", the point at

which the metal and barrier layers over the insulating layer have just been cleared from the surface of the insulating layer.

5 Since it is very difficult to determine and stop at the "just clear point", a planarization polishing process is proposed wherein there are two steps of polishing. In the first step any non-selective polishing composition which will have high removal rates for the metal may be used. It may have either high or low removal rates for the barrier layer and the  
10 insulating layer because the first step process will be stopped just before or just as the metal layer is entirely removed. The second step polishing process will use a slurry for which there is lower selectivity between the metal and the insulating layer, preferably between 10:1 and 1:10 and more preferably between 3:1 and 1:3, and most preferably about 1:1.

15 It has surprisingly been found that slurries comprised of colloidal silica particles with a primary particle size of 10 to 100 nanometers and a surface area of 20 to 600 m<sup>2</sup>/g provide second step selectivities within the desired range as well as a low level of scratches on the insulating layer  
20 surface, little erosion of the insulating layer surface, and little dishing of the metal surface.

As used in this specification, "primary particle size" is intended to mean the distance of the non-agglomerated or non-aggregated particle's  
25 largest dimension (either height, length or width).

The surface area of the particles can be measured by the nitrogen adsorption method of S. Brunauer, P. H. Emmet and I. Teller, J. Am. Chemical Society, Volume 60, page 309 (1938) which is commonly  
30 referred to as BET measurement.

The slurries useful for this invention also comprise an oxidizing agent. Common oxidizing agents are nitrates, iodates, chlorates, perchlorates, chlorites, sulphates, persulphates, peroxides, ozonated water,  
35 and oxygenated water. Oxidizing agents can be used in slurries for CMP at concentrations of about 0.01% to about 7% by weight. Generally they are used at concentrations of about 1% to about 7% by weight. An iodate is a preferred oxidizing agent.

Dielectric oxide complexing agents which act to suppress the rate of removal of the dielectric oxide surface are described and claimed in US Patents Nos. 5,391,258; and 5,476,606 which are made part of this specification by reference. Farkas et al. in US Patent No. 5,614,444 disclose slurry additives which have a polar component and an apolar component. These additives passivate the dielectric surface and reduce its rate of removal. This patent (USP 5,614,444) is also made a part of this specification by reference.

Compounds which act as complexing agents or chelating agents for  $\text{SiO}_2$  as described in U. S. Patent 5391258 and U. S. Patent 5476606 must have at least two acid groups present in the structure which can affect complexation to the oxide surface. Acid species are defined as those functional groups having a dissociable proton. These include, but are not limited to, carboxylate, hydroxyl, sulfonic and phosphonic groups. Carboxylate and hydroxyl groups are preferred as these are present in the widest variety of effective species. Particularly effective are structures which possess two or more carboxylate groups with hydroxyl groups in an alpha position, such as straight chain mono- and di-carboxylic acids and salts including, for example, malic acid and malates, tartaric acid and tartarates and gluconic acid and gluconates. Also effective are tri- and polycarboxylic acids and salts with secondary or tertiary hydroxyl groups in an alpha position relative to a carboxylic group such as citric acid and citrates. Also effective are compounds containing a benzene ring such as ortho di- and polyhydroxybenzoic acids and acid salts, phthalic acid and acid salts, pyrocatecol, pyrogallol, gallic acid and gallates and tannic acid and tannates. In the examples which follow a phthalate is used as the complexing agent.

It is believed that any surfactant, whether it be an anionic, cationic, non-ionic or zwitter-ionic surfactant, might be effective in the compositions of this invention.

Surfactants and complexing agents may be used in slurries for CMP at about 0.1% to about 7% by weight. Preferably they are used at about 0.5% to about 4% by weight.

Since the barrier layer is so thin, the rate of removal of barrier layer material can range anywhere from about 20 Angstroms/minute up to 2000

Angstroms/ minute or greater. The rates of removal of the metal layer and the insulating layer may be moderate to high (about 300 to about 2000 angstroms/minute) as long as the selectivity between them is in the range of 10:1 to 1:10.

### EXAMPLE

Tungsten sheet wafers and thermal oxide wafers were polished on a Westech 372 Polisher (available from IPEC Planar, Phoenix, AZ) on which an IC-1400-K Grooved pad (available from Rodel, Inc., Newark, DE) was used. Polishing conditions were: down force, 7.5 psi; table, 35 rpm; carrier, 35 rpm; slurry flow, 200 ml/min; polishing time, 2 min; rinse, 30 sec (polishing with DI water). The slurry comprised an abrasive at a concentration as listed below. The chemical part of the slurry comprised an oxidizing agent (an iodate at about 1% to about 7%) and a compound which complexes with dielectric oxide silica (a phthalate at about 2% to about 4%). The following table shows polishing rates for tungsten and the silicon oxide insulating material.

Table 1

No.	Abrasive	Wt. %	Primary Particle Size, nm	Surface Area, m <sup>2</sup> /g	W RR, Å/min	SiO <sub>2</sub> RR, Å/min	Selectivity W:SiO <sub>2</sub>
1	fumed Al <sub>2</sub> O <sub>3</sub>	5			1440	37	39:1
2	fumed Al <sub>2</sub> O <sub>3</sub>	10			1434	50	29:1
3	fumed silica	5	20	65-100	1070	8	135:1
4	fumed silica	10	20	65-100	1242	7	175:1
5	colloidal Al <sub>2</sub> O <sub>3</sub>	5			1527	7	232:1
6	colloidal silica	5	50	40-60	494	581	1:1
7	colloidal silica	10	50	40-60	721	890	1:1

8	colloidal silica	10	50	40-60	1236	1646	1:1
9	colloidal silica	10	12	180-230	1847	887	2:1

It is obvious from the above Table that colloidal silica abrasive provides the desired rates and selectivities for the second step process of this invention. A fumed silica with the tested oxidation chemistry and pH,

even in the same size range and range of surface area, does not give the desired rates and selectivities. The alumina abrasives, fumed and colloidal, do not provide the desired rates and selectivities.

Metal layers for which the process and slurries of this invention might be useful include, but are not limited to, tungsten, aluminum, copper, platinum, palladium, gold, iridium and any combination or alloy thereof.

Barrier layers for which the process and slurries of this invention might be useful include, but are not limited to, tantalum, tantalum nitride, titanium, titanium nitride, and any combinations thereof.

Insulating or dielectric layers for which the process and slurries of this invention might be useful include, but are not limited to, PSG, BPSG, TEOS, SiO<sub>2</sub>, and any low-K polymeric material.

Depending on the chemicals used, the slurries of this invention may have a pH anywhere in the acidic, neutral, or alkaline range.



**CLAIMS**

- 5 1. A composition useful for a second step planarization of a metal, barrier layer, and a dielectric insulating layer structure comprising: water, colloidal silica particles with a primary particle size between 10 and 100 nanometers and a surface area of 20 to 600 m<sup>2</sup>/g, and an oxidizing agent.
- 10 2. A composition according to claim 1 wherein said oxidizing agent is from the group consisting of nitrates, iodates, chlorates, perchlorates, chlorites, sulphates, persulphates, peroxides, ozonated water, and oxygenated water.
- 15 3. A composition according to claim 2 wherein said oxidizing agent is an iodate.
- 20 4. A composition according to claim 1 further comprising a surfactant.
- 25 5. A composition according to claim 1 further comprising a compound which acts to suppress the rate of removal of the dielectric layer.
- 30 6. A composition according to claim 5 wherein said compound which acts to suppress the rate of removal of the dielectric layer is a phthalate.
- 35 7. A second-step planarization process for a metal, barrier layer, and dielectric insulating layer structure on a semiconductor wafer comprising:
  - (a) positioning said wafer in a polishing machine comprised of a polishing pad and a carrier for said wafer,
  - (b) contacting said wafer and said pad while maintaining a relative motion between said pad and said wafer and while a polishing composition is supplied to the interface between said wafer and said polishing pad,said polishing composition comprising: water, colloidal silica particles with a primary particle size between 10 and 100
- 40

nanometers and a surface area of 20 to 600 m<sup>2</sup>/g, and an oxidizing agent.

- 5       **8.** A method according to claim 7 wherein said oxidizing agent is from the group consisting of nitrates, iodates, chlorates, perchlorates, chlorites, sulphates, persulphates, peroxides, ozonated water, and oxygenated water.
- 10       **9.** A method according to claim 8 wherein said oxidizing agent is an iodate.
- 15       **10.** A method according to claim 7 wherein said composition further comprises a surfactant.
- 11.** A method according to claim 7 wherein said composition further comprises a compound which acts to suppress the rate of removal of the dielectric layer.
- 20       **12.** A method according to claim 11 wherein said compound which acts to suppress the rate of removal of the dielectric layer is a phthalate.